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### (54) PROCESS IN ASSOCIATION WITH PULP BLEACHING

VERFAHREN IN ZUSAMMENHANG MIT DEM ZELLSTOFFBLEICHEN

PROCEDE ASSOCIE AU BLANCHIMENT DE PATE DE CELLULOSE

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**Description**

The invention relates to a process for chlorine-free bleaching of chemical pulp in association with production of the same, in which a suspension of the pulp has a consistency exceeding 8% of cellulose-containing fibre material and in which the pulp entering into a bleaching line is fed continuously through at least one bleaching vessel in the bleaching line, is treated with at least one acid for adjusting the pH to a value below 7 and with a chelating agent, and is subsequently bleached in at least one stage to a brightness exceeding 80% ISO, using hydrogen peroxide or a corresponding quantity of another peroxide, added in a quantity exceeding 5 kg/BDMT.

Marketing and environmental considerations have demanded that extensive efforts be made to eliminate the use of chlorine-containing compounds for bleaching purposes. Using current technology, it is difficult to achieve complete bleaching of paper pulp prepared from soft wood sulphate pulp using oxygen, hydrogen peroxide and ozone.

There are a number of peroxide bleaching processes of the Lignox and Macrox type in which a combination of EDTA treatment and peroxide addition is used. These processes require a minimum of a 4-hour reaction time at 90°C and, despite this, it is found that when a successful bleaching of oxygen-delignified softwood pulp has been carried out, with the pulp having a kappa of 12 and with a brightness of 77-79 ISO having been achieved, about half of the quantity of peroxide employed remains unused. The intention is that the latter should subsequently be returned to the process for reuse after the addition of fresh peroxide. As far as we know, this still does not take place on a factory scale. In some cases, the peroxide is returned to the oxygen reactor, with any possible brightness-increasing effect being negligible.

Through the SE-A-8503153-2 (Wagner-Biro AG), a process is known for delignifying pulp using oxygen and/or ozone with the possible addition of peroxide. In the said process, the pulp is placed in contact with oxygen, possibly in the presence of peroxide, at a temperature of 80°C to 150°C. An alkalisng supplement is then added to the pulp. The process can be repeated in several stages with increasing pressures and/or temperatures. This process is based on a two-stage process where the first stage takes place, in this case, at a consistency of 2.5-4.5% and the second stage is carried out at a consistency of 10%. The quantity of peroxide employed is 0.5 kg of H<sub>2</sub>O<sub>2</sub> per kg of ptp.

An approach which might seem to present itself immediately would be to raise the temperature and apply pressure in order to shorten the necessary reaction time and/or decrease the peroxide residue in order to achieve optimal utilisation of the hydrogen peroxide employed, and this suggestion is in fact included as a possibility in the SE-A-8902058-0 (EKA Nobel AB) which corresponds to EP-A-0 402 335, in which the so-called Lignox process is described. Experiments in this direction have been carried out, but have failed, the results in all respects being worse than those achieved with purely atmospheric peroxide bleaching. It has even been suggested that oxygen is of no value in bleaching by the Lignox method. The application of pressure is preferably carried out using an MC pump, with the pumped suspension having a consistency exceeding 8% and preferably less than 18%.

It should be noted that experiments to which reference has been made in the patent and other literature have, for understandable reasons, been carried out on a laboratory scale. Indications have been obtained that the results are worse if the temperature is increased (for example from 90°C to 95°C) and the conclusion has been drawn that peroxide bleaching should preferably take place at a temperature below 90°C.

The object of the present invention is to produce a process of the type mentioned in the introduction which provides efficient and more homogeneous bleaching.

This is achieved, according to the invention as disclosed in claim 1, by the peroxide bleaching taking place at elevated temperature exceeding 90°C and at a pressure in the bleaching vessel which exceeds 2 bar, by the cross-sectional area of the bleaching vessel exceeding 3 m<sup>2</sup>, and by the area of the metal surface exposed towards the interior of the bleaching vessel being less than 4V m<sup>2</sup>, where V indicates the volume of the vessel in m<sup>3</sup>.

It can be added that, in laboratory bleachings, plastic bags are used under conditions of atmospheric pressure in a waterbath whose temperature is maximally 90°C-95°C. For obvious reasons, pressurised procedures in a gas atmosphere are carried out in acid-resistant autoclaves.

It has now emerged, surprisingly, that the hot metal surface of the autoclave catalyses decomposition of the peroxide. Brightness, kappa number and viscosity all reach improved values in association with lower consumption of peroxide if the pulp and the peroxide are placed together in a sealed plastic bag before the bag is put into the autoclave which is filled with water for heat transfer between the autoclave and the bag. Experiments have been carried out both with and without the application of an extra (5 bar) oxygen pressure. Without entirely espousing a particular theory, it can be supposed that a plausible mechanism for this could be that the hot metal surfaces of the autoclave catalyse decomposition of the peroxide. To investigate this, the experiments described below, inter alia, were carried out. These experiments demonstrated that our assumption was correct. Since the quantity of inwardly exposed metal surface per unit of volume in a vessel decreases quadratically with regard to the increase in volume of the vessel, we have been able to conclude that the above-mentioned problem is laboratory-specific, i.e. at a particular value of the cross-sectional area of the bleaching vessel (circa 3 m<sup>2</sup>, which effect consequently decreases further with increased cross-sectional area - D) this effect is marginal.

It has also emerged surprisingly that a further improve of the process according to the invention is obtained by using

a complexing agent which is capable of withstanding higher pH values without being broken down. With higher pH values is meant values up to 11.

It is known within the state of the art to wash the pulp suspension after the complexing agent, e.g. EDTA, has been added in the Q stage, in order first to bind and then to wash out the transition elements present in the pulp suspension.

5 A certain amount of the metal bound by the EDTA, however, will remain in the suspension and be carried over into the next stage. Moreover, there may still be metal not bound by the EDTA which also remains.

At the pH values existing in the next stage it appears that the metals complexly bound by EDTA will be freed since EDTA does not withstand the pH values used in the bleaching stage. The freed metal ions, as well as those never bound, have a detrimental effect on the continued process since they decompose the peroxide used in the bleaching.

10 Thus it has proved to be an improvement to the process according to the invention, after the Q-stage, preferably together with the peroxide, to add an amount of a complexing agent, which is capable of withstanding high pH-values without decomposition. By this addition the disadvantages referred to above will be removed. According to the invention a preferred complexing agent is DTPA.

15 It has also emerged that a further improvement of the process according to the invention is obtained by supplying oxygen, in conjunction with the bleaching, in a quantity which is less than 5 kg/BDMT, preferably less than 3 kg/BDMT and more preferably less than 1 kg/BDMT. It has also been found that nitrogen can be used instead of oxygen, resulting in only a small increase in the consumption of peroxide.

According to a further aspect of the invention, the process is improved by the temperature during the bleaching equalling or exceeding 100°C, and more preferably being between 100°C and 105°C.

According to a further aspect of the invention, the process is improved by the quantity of peroxide employed exceeding 10 kg/BDMT and being less than 35 kg/BDMT in order to achieve a brightness exceeding 85 ISO.

According to a further aspect of the invention, the process is improved by the pressure exceeding 3 bar, preferably being within the interval 5 to 15 bar and more preferably within the interval 5 to 10 bar.

25 According to a further aspect of the invention, the process is improved by the pulp, during the bleaching, not being permitted to any significant extent to come into contact with metal surfaces, with preferably at least the inner surface of the bleaching vessel being made of some polymeric or ceramic material.

According to a further aspect of the invention, the process is improved by the Q stage being preceded by a Z stage or by a peracetic acid stage and by a brightness exceeding 85 ISO being obtained with the aid of such a 2-stage process in association with a consumption of peroxide which is less than 20 kg/BDMT.

30 According to a further aspect of the invention, the process is improved by no washing taking place between ZQ, and preferably by an A stage preceding the Z stage.

According to a further aspect of the invention, the manganese content should be less than 5 g/BDMT of pulp, preferably less than 1 g/BDMT of pulp, and more preferably less than 0.5 g/BDMT of pulp, in the pulp for the peroxide stage, which is largely the same as the content in the finally bleached pulp.

35 According to a further aspect of the invention, the process is improved by, at the bleaching stage, a pH-elevating agent first being added to the pulp suspension prior to the peroxide being mixed in at a temperature of less than 90°C, before the temperature is finally raised to the desired level for carrying out the bleaching itself.

According to a further aspect of the invention, the process is improved by, at addition of the pH-elevating agent to the pulp suspension in the bleaching stage preceding the addition of the peroxide, the initial pH-value not being raised higher than to 11.5, preferably the pH-value is adjusted to a value between 10 and 11.

According to a further aspect of the invention, the process is improved by at least one complexing agent participating in the peroxide bleaching stage, which complexing agent preferably is added to the suspension together with the peroxide.

45 According to a further aspect of the invention, the process is improved by one of the at least one complexing agents being one, which substantially withstands a pH-value up to 11, this complexing agent preferably being DTPA.

According to a further aspect of the invention, the process is improved by the complexing agent DTPA being added in an amount preferably between 1 and 2 kg DTPA/ADMT

According to a further aspect of the invention, the process is improved by the positive pressure in the bleaching vessel being obtained with the aid of a centrifugal pump, a so-called MC pump.

50 According to a further aspect of the invention, the process is improved by the peroxide bleaching being carried out hydraulically, with no gas phase being present in the bleaching vessel.

According to a further aspect of the invention, the process is improved by the diameter of the bleaching vessel exceeding 3 metres, preferably 5 metres and more preferably 7 metres.

The examples below illustrate the invention and demonstrate the surprising and unexpected result.

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### Comparative experiments

In conjunction with the description below, reference is also made to the accompanying diagrams where:

Fig. 1. shows a diagram of the relationship, during bleaching according to the invention, between brightness, %ISO and total consumption of  $H_2O_2$  kg/ADMT, at either 5 bar and 100°C or 5 bar and 110°C for 1, 2 and 3 hours, and at 90°C, 0 bar and 4 hours, and at 90°C, 5 bar and 4 hours.

Fig. 2. shows a diagram of the relationship, during bleaching according to the invention, between brightness %ISO and viscosity,  $dm^3/kg$ , at either 5 bar and 100°C or 5 bar and 110°C for 1, 2 and 3 hours, and at 90°C, 0 bar and 4 hours, and at 90°C, 5 bar and 4 hours.

Fig. 3. shows a diagram of the relationship between brightness, %ISO, and total consumption of  $H_2O_2$ , kg/ADMT, during bleaching with a pressurised P stage according to the invention inserted in different bleaching sequences and with an ozone stage at 50°C including a pressure of 6 kg or 4 kg and varying quantities of manganese.

Fig. 4. shows a diagram (the same experimental series) of the relationship between brightness, %ISO, and viscosity,  $dm^3/kg$ , during bleaching with a pressurised P stage according to the invention inserted in different bleaching sequences and with an ozone stage at 50°C including a pressure of 6 kg or 4 kg and varying quantities of manganese.

Fig. 5. shows a diagram of the relationship between brightness, %ISO, and reaction time for a bleaching sequence with a pressurised (PO) stage after a (QZ) stage according to the invention and a sequence for comparison at atmospheric pressure and 90°C.

Fig. 6. shows a diagram of the relationship between brightness, %ISO, and viscosity,  $dm^3/kg$ , for the bleaching sequence in Fig. 5. according to the invention and a sequence for comparison at atmospheric pressure and 90°C.

Fig. 7. shows a diagram of the relationship between brightness, %ISO, and total consumption of  $H_2O_2$ , kg/ADMT, for the bleaching sequence in Fig. 5. according to the invention and a sequence for comparison at atmospheric pressure at 90°C.

Fig. 8. shows a diagram of the relationship between brightness, %ISO, and reaction time for a bleaching sequence with a pressurised (PO) stage according to the invention and a sequence for comparison at atmospheric pressure and 90°C.

Fig. 9. shows a diagram of the relationship between brightness, %ISO, and viscosity,  $dm^3/kg$ , for a bleaching sequence in Fig. 8. according to the invention and a sequence for comparison at atmospheric pressure and 90°C.

Fig. 10. shows a diagram of the relationship between brightness, %ISO, and total consumption of  $H_2O_2$ , kg/ADMT, for the bleaching sequence in Fig. 8. according to the invention and a sequence for comparison at atmospheric pressure and 90°C.

Fig. 11. Shows two diagrams of the relationship between brightness, %ISO, and viscosity,  $dm^3/kg$ , for pressurized (PO)-bleaching with either the standard Q pretreatment or the pretreatment using DTPA according to the invention. The first diagram shows bleaching of softwood the other one of softwood kraftpulp.

Fig. 12. shows a diagram of the influence of protectors (e.g. complexing agents) on the relationship between brightness, %ISO, and total consumption of  $H_2O_2$ , kg/ADMT, for a Q(PO)-bleaching of a lab. delignified pulp, and the relationship viscosity,  $dm^3/kg$ , to brightness, %ISO, for the same.

#### 40 Q(Pressurised P)-bleaching of oxygen-delignified soft wood pulp

In order to demonstrate the effect of, on the one hand, the difference from pulp suspension which is bleached in direct contact with metal surfaces in the bleaching vessel and of, on the other hand, the effect of applying a pressure, as well as indirectly the effect of raising the temperature during the process, since when the autoclaves are filled with water round the plastic bags a much improved heat transfer to the pulp suspension is obtained, the following experiments were carried out.

45 A pulp with a kappa number of 12.1, a consistency of 10% and a viscosity of 1020  $dm^3/kg$ , was treated with EDTA in a Q stage, temperature 70°C, initial pH ( $H_2SO_4$ ) 4.7 and a final pH equal to 5.0. The pulp treated in this way was subsequently subjected to an EOP stage at a consistency of 10% and during a period of 240 min and at the temperature of 90°C. This stage was carried out under normal pressure column a, b and c, as well as with 5 bar of positive pressure (oxygen atmosphere). The result is shown in the table below.

TABLE I

	a	b	c	d	e	f
Consistency, %			10			
Temperature, °C			90			
Time, minutes			240			
Average pressure, bar (excess)	*	**	****	*	**	***
MgSO <sub>4</sub> , kg/BDMT	0	0	0	5	5	5
H <sub>2</sub> O <sub>2</sub> , kg/BDMT	3	3	3	3	3	3
NaOH, kg/BDMT	35	35	35	35	35	35
Consumption of H <sub>2</sub> O <sub>2</sub> , kg/BDMT	25	25	25	25	25	25
Final pH	33.0	26.4	25.7	33.3	23.7	25.3
Kappa number	11.2	10.9	10.9	11.1	10.8	10.8
Viscosity, dm <sup>3</sup> /kg	4.8	4.7	4.6	4.5	4.3	4.2
Brightness, % ISO	746	849	828	802	838	837
Quantity of peroxide employed, kg/ADMT	77.9	78.5	79.7	79.7	80.7	81.6
Consumption of peroxide, kg/ADMT	33	33	33	33	33	33

\* in autoclaves with direct contact with the metal

\*\* sealed in plastic bags and introduced into the  
autoclaves

\*\*\* sealed in plastic bags and introduced into the  
autoclaves filled with water for improved heat  
transfer

Although the applied temperature of 90°C lies outside the scope of claim 1, it can be seen from Table I that the absence of contact between the pulp suspension and the metal surfaces directly affects the consumption of H<sub>2</sub>O<sub>2</sub> and that the latter is also affected by the supply of heat to the pulp suspension, which can be seen from a comparison between columns b and c.

It is evident from Table 1 that the application of oxygen pressure (5 bar) improves the brightness by two units and gives better selectivity and a kappa reduction, which can be seen from the above table by comparing columns c and f.

Increasing the temperature by 10°C from 90°C to 100°C approximately halves the reaction time required to achieve the same final brightness when using the same loading. This is shown in further experiments on the same pulp as in the above experiments. In this case all the experiments were carried out using an applied oxygen pressure of 5 bar.

The experimental parameters and results are recorded in Table II below. By comparing I:f with II:e the temperature effect can be demonstrated.

TABLE II

	a	b	c	d	e	f
Consistency, %			10			
Temperature, °C			100			
Time, minutes	60	120	180	60	120	180
Average pressure, bar (excess)	5	5	5	5	5	5
MgSO <sub>4</sub> , kg/BDMT	3	3	3	3	3	3
H <sub>2</sub> O <sub>2</sub> , kg/BDMT	25	25	25	35	35	35
NaOH, kg/BDMT	24	24	24	25	25	25
Consumption of H <sub>2</sub> O <sub>2</sub> , kg/BDMT	12.2	16.0	19.1	16.4	21.4	26.0
Final pH	10.8	10.6	10.4	10.7	10.5	10.4
Kappa number	5.3	4.6	4.2	5.0	4.3	4.0
Viscosity, dm <sup>3</sup> /kg	906	829	803	896	827	790
Brightness, % ISO	73.8	79.6	81.4	76.9	81.3	83.1
Quantity of peroxide employed, kg/ADMT	23	23	23	33	33	33
Consumption of peroxide, kg/ADMT	11	15	18	15	20	24

From the above Table II (II:e and II:c), it can also be seen that lowering the quantity of peroxide employed from 35 to 25 kg ptp (2/3) increases the reaction time which is required to achieve a brightness of 81.4 ISO from 2 to 3 hours, i.e. by lengthening the reaction time an economy can be achieved in the quantity of peroxide employed.

#### Comparative experiments at different temperatures.

TABLE III

	a	b	c	d	e
Consistency, %		10			
Temperature, °C	90	90	100	100	110
Time, minutes			240		
Average pressure, bar (excess)	0	5	0	5	5
MgSO <sub>4</sub> , kg/BDMT	3	3	3	3	3
H <sub>2</sub> O <sub>2</sub> , kg/BDMT	35	35	35	35	35
NaOH, kg/BDMT	30	30	30	30	30
Consumption of H <sub>2</sub> O <sub>2</sub> , kg/BDMT	33.0	31.1	34.8	34.9	34.9
Final pH	11.4	11.3	11.1	11.3	10.0
Kappa number	4.6	4.4	4.4	3.5	3.9
Viscosity, dm <sup>3</sup> /kg	707	733	660	685	675
Brightness, % ISO	77.4	81.4	76.4	80.6	80.8
Quantity of peroxide employed, kg/ADMT	33	33	33	33	33
Consumption of peroxide, kg/ADMT	31	29	32	32	32

- in autoclaves with direct contact with the metal  
 - note the effect of oxygen pressure

In addition to this, further experiments have been carried out on the same pulp at oxygen pressures of 0-10 bar in order to demonstrate the importance of the temperature in combination with the oxygen pressure.

From the graph shown in Fig. 1, it can be seen, inter alia, that a Q(pressurised P)-sequence at 110°C and 5 bar decreases the necessary reaction time from 4 hours to 1 hour as compared with that which is required under conventional atmospheric conditions at 90°C. In addition, the peroxide consumption which is necessary decreases by 25% to 18 kg ptp.

From the graph in Fig. 2 it can be seen, inter alia, that simply applying oxygen pressure at 90°C increases the brightness by 2 steps from ~ 80 to ~ 82.

It has now emerged that there is a possibility of dividing the pressurised-P stage into two stages, with the first part of the process taking place, for example, at a lower temperature of 80-90°C under atmospheric pressure and the second part taking place under applied oxygen pressure at 110-120°C, once the content of peroxide present in the pulp has declined.

The importance of a Q treatment prior to a peroxide stage is already well known. If ozone is combined with the pressurised P stage, a simple 2-stage sequence can be used to produce marketable pulp of full brightness (88-90 ISO) and with good strength properties. See Fig. 3, where the total consumption of hydrogen peroxide has been related to the brightness in % ISO, and Fig. 4., where the viscosity has been related to the brightness in % ISO. The correlation between Mn content, brightness and hydrogen peroxide consumption or viscosity for a number of different sequences can clearly be seen in these graphs. As is evident from the sequence ZQ, the sequence ozone followed by a Q stage together with alkali, pH 5-6, without interpolated washing is consequently favourable for producing a low manganese content and good results.

The importance of the presence of manganese for peroxide consumption and pulp viscosity has been found to be crucial. Our experiments have demonstrated that every additional gram of manganese/BDMT of pulp increases the peroxide consumption by 2 kg/BDTM and lowers the quality of the pulp by 10 to 20 units in the SCAN viscosity (dm<sup>3</sup>/kg). The degree of washing must exceed 95%, preferably 99%, in order to achieve these low manganese contents. It is best to use one or more, or a combination of, KAMYR atmospheric diffusers, KAMYR pressure diffusers or KAMYR washing presses in the bleaching line.

The appreciable advantages of having the pressurised (PO) stage after a (ZQ) stage, compared with conventional technology under atmospheric pressure, are evident from the graph in Fig. 5, where a decreased reaction time can be observed, from the graph in Fig. 6, where the process using a pressurised bleaching with peroxide and ozone leads to appreciably lower loss of viscosity, i.e. results in the achievement of higher pulp viscosity and higher brightness in relation to the reference experiment, and from the graph in Fig. 7 which demonstrates that, to achieve a brightness of 88-89 % ISO according to the invention, the consumption of peroxide is halved as compared with reference experiments carried out under atmospheric pressure.

Comparative experiments have also been carried out (see Figs. 8, 9 and 10) with regard to pressurised-(PO) bleaching of oxygen-delignified Euc. globulus, hardwood pulp, at 105°C, and bleaching of the same pulp under atmospheric pressure and at 90°C. The pulp having a kappa number of 7.2 was subjected to a preceding Q stage and the quantity of peroxide fed in was 33 kg/ptp.

Comparative experiments have also been carried out (see Fig 11) to show the influence on viscosity on two different softwood pulps in the pressurized (PO) stage bleaching from standard Q pretreatment and a pretreatment with DTPA, resp. One may note that the same brightness is reach in both cases in 3, resp. 4 hours and at the same viscosities.

Comparative experiments have also been carried out (see Fig 12) to show the influence on viscosity as related to brightness and the consumption of H<sub>2</sub>O<sub>2</sub> as related to brightness for different combinations in the (PO) stage. In the first diagram one may note the decrease in consumption of the peroxide adding DTPA, as compared to the addition of MgSO<sub>4</sub> alone.

The diagram also shows that MgSO<sub>4</sub> has been used. To use Mg as well as Ca, alone or in combination, in the process in order to improve the quality of the pulp, is known to the skilled man.

In the diagram below on may note the beneficial effects on the viscosity at the same brightness using the combination as above

The object of the invention is to achieve a high degree of utilisation of the peroxide employed and at the same time to achieve a high degree of brightness in the product. As we have found out, this can be affected separately by a number of measures as have been explained in the foregoing.

## Claims

1. Process for chlorine-free bleaching of chemical pulp in association with the production thereof, where a suspension of the pulp has a concentration exceeding 8% of cellulose-containing fibre material, where a pulp entering into a bleaching line is fed continuously through at least one bleaching vessel in the bleaching line, is treated with at least one acid for adjusting the pH to a value below 7, and with a chelating agent, and is thereafter bleached in at least one stage to a brightness exceeding 80%ISO, with hydrogen peroxide or a corresponding quantity of another peroxide, employed in a quantity exceeding 5 kg/BDMT, characterized in that the peroxide bleaching is effected at a temperature exceeding 90° C and at a pressure in the bleaching vessel which exceeds 2 bar and in that the cross-sectional area of the bleaching vessel exceeds 3 m<sup>2</sup>, and in that the area of the metal surface exposed towards the interior of the bleaching vessel is less than 4V m<sup>2</sup>, where V indicates the volume of the vessel in m<sup>3</sup>.

2. Process according to Patent Claim 1, **characterized** in that, in connection with the bleaching, oxygen is added in a quantity which is less than 5 kg/BDMT, preferably less than 3 kg/BDMT and more preferably less than 1 kg/BDMT.

5 3. Process according to any one of the preceding claims, **characterized** in that the temperature during the bleaching is equal to or exceeds 100°C and more preferably is between 100°C and 105°C.

10 4. Process according to any one of the preceding claims, **characterized** in that the quantity of peroxide employed exceeds 10 kg/BDMT and is less than 35 kg/BDMT for achieving a brightness exceeding 85 ISO.

15 5. Process according to any one of the preceding claims, **characterized** in that the pressure exceeds 3 bar, preferably is within in the interval 5 to 15 bar and more preferably is within the interval 5 to 10 bar.

6. Process according to any one of the preceding claims, **characterized** in that the pulp suspension during the bleaching is not permitted to any significant extent to come into contact with metal surfaces, with preferably at least the inner surface of the bleaching vessel being made of some polymeric or ceramic material.

20 7. Process according to any one of the preceding claims, **characterized** in that the Q stage with the chelating agent is preceded by a Z stage or by a peracetic acid stage and in that a brightness exceeding 85 ISO is obtained using such a 2-stage process in association with a consumption of peroxide which is less than 20 kg/BDMT.

25 8. Process according to Patent Claim 7, **characterized** in that no washing takes place between ZQ, and preferably in that an A stage with an acid precedes the Z stage.

9. Process according to Patent Claim 3, **characterized** in that, at the bleaching stage, a pH-elevating agent is first added to the pulp before the peroxide is mixed in at a temperature which is less than 90°C, before the temperature is finally raised to the desired level for carrying out the bleaching itself.

30 10. Process according to Patent Claim 9, **characterized** in that, at the addition of the pH-elevating agent to the pulp suspension in the bleaching stage the initial pH-value is raised no higher than to 11.5, preferably to a value between 10 and 11.

11. Process according to any one of the preceding claims, **characterized** in that at least one complexing agent is participating in the peroxide bleaching stage, which complexing agent preferably is added to the suspension together with the peroxide.

35 12. Process according to any one of the preceding claims, **characterized** in that one of the at least one complexing agents being one, which substantially withstands a pH-value up to 11, this complexing agent preferably being DTPA.

13. Process according to any one of the preceding claims, **characterized** in that DTPA being is added in an amount of preferably between 1 and 2 kg DTPA/ADMT.

40 14. Process according to any one of the preceding claims, **characterized** in that the positive pressure in the bleaching vessel is obtained with the aid of a centrifugal pump, a so-called MC pump.

15. Process according to any one of the preceding claims, **characterized** in that the peroxide bleaching is carried out hydraulically, with no gas phase being present in the bleaching vessel.

45 16. Process according to any one of the preceding claims, **characterized** in that the diameter of the bleaching vessel exceeds 3 metres, preferably 5 metres and more preferably 7 metres.

17. Process according to any one of the preceding claims, **characterized** in that the manganese content is less than 5 g/BDTM of pulp, preferably less than 1 g/BDTM of pulp and more preferably less than 0.5 g/BDMT of pulp, in the pulp supplied to the peroxide stage, which content is largely the same as the content in the finally bleached pulp.

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#### Patentansprüche

1. Verfahren zum chlorfreien Bleichen von Chemie-Zellstoff in Verbindung mit der Erzeugung desselben, wobei eine

Suspension des Zellstoffs eine Stoffdichte, die einen Gehalt von 8% zellulosehaltigem Fasermaterial überschreitet, aufweist, wobei ein in eine Bleichstrecke einlaufender Zellstoff, der kontinuierlich durch wenigstens ein Bleichgefäß in der Bleichstrecke geführt wird, mit wenigstens einer Säure zur Einstellung des pH auf einen Wert unter 7 und mit einem Chelatbildner behandelt und nachher in wenigstens einer Stufe bis zu einer Helligkeit, die übersteigt, mit Wasserstoffperoxid oder einer entsprechenden Menge eines anderen Peroxids eingesetzt in einer 5 kg/BDMT (BDMT=staubtrockene metrische Tonne) übersteigenden Menge, gebleicht wird, dadurch gekennzeichnet, daß die Peroxidbleiche bei einer Temperatur die 90°C übersteigt und einem Druck im Bleichgefäß, der 2 bar übersteigt, durchgeführt wird und daß die Querschnittsfläche des Bleichgefäßes 3 m<sup>2</sup> übersteigt und daß das Quadratmaß der Metalloberfläche, die gegen das Innere des Bleichgefäßes freiliegt, weniger als 4V m<sup>2</sup> beträgt, wobei V das Volumen des Gefäßes in m<sup>3</sup> angibt.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß in Verbindung mit dem Bleichen Sauerstoff in einer Menge, die geringer als 5 kg/BDMT, bevorzugt geringer als 3 kg BMDT, und mehr bevorzugt geringer als 1 kg/BDMT ist, zugesetzt wird.

3. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Temperatur während der Bleiche gleich oder mehr als 100°C beträgt, und mehr bevorzugt zwischen 100°C und 105°C liegt.

4. Verfahren nach einem der vorhergehenden den Ansprüche, dadurch gekennzeichnet, daß die Menge an eingesetztem Peroxid 10 kg/BDMT übersteigt und weniger als 35 kg/BDMT beträgt um eine 85 ISO übersteigende Helligkeit zu erreichen.

5. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Druck 3 bar übersteigt, bevorzugt innerhalb des Bereiches von 5 bis 15 bar liegt und mehr bevorzugt innerhalb des Bereiches von 5 bis 10 bar liegt.

6. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß es der Zellstoffsuspension während der Bleiche nicht gestattet ist, in einem irgendwie signifikanten Ausmaß mit Metallflächen in Berührung zu gelangen, wobei vorzugsweise wenigstens die Innenfläche des Bleichgefäßes aus einem polymeren oder keramischen Material gefertigt ist.

7. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Q-Stufe mit dem Chelatbildner eine Z-Stufe oder eine Peressigsäurestufe vorhergeht und eine 85 ISO übersteigende Helligkeit erzielt wird, wenn ein solches Zweistufenverfahren in Verbindung mit einem Peroxidverbrauch, der geringer ist als 20 kg/BDMT, angewendet wird.

8. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß zwischen ZQ kein Waschen stattfindet und daß vorzugsweise der Z-Stufe eine A-Stufe mit einer Säure vorhergeht.

9. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß bei der Bleichstufe zuerst ein pH-erhöhendes Mittel dem Zellstoff zugesetzt wird, bevor das Peroxid bei einer Temperatur, die weniger als 90°C beträgt, eingemischt wird, bevor die Temperatur schließlich auf den gewünschten Wert erhöht wird, um die Bleiche selbst durchzuführen.

10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß beim Zusatz des pH-erhöhenden Mittels zur Zellstoffsuspension in der Bleichstufe der anfängliche pH-Wert auf nicht höher als auf 11,5, vorzugsweise auf einen Wert zwischen 10 und 11, angehoben wird.

11. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß wenigstens ein Komplexbildner an der Peroxid-Bleichstufe teilnimmt, welcher Komplexbildner vorzugsweise zusammen mit dem Peroxid der Suspension zugegeben wird.

12. Verfahren nach einem der vorhergehenden Ansprüche dadurch gekennzeichnet, daß einer des wenigstens einen Komplexbildners ein solcher ist, der im wesentlichen gegen einen pH-Wert bis 11 beständig ist, wobei dieser Komplexbildner vorzugsweise DTPA ist.

13. Verfahren nach einem der vorhergehenden Ansprüche dadurch gekennzeichnet, daß die DTPA in einer Menge von vorzugsweise zwischen 1 und 2 kg DTPA/ADMT (ADMT=lufttrockene metrische Tonne) zugesetzt wird.

14. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der positive Druck im Bleichgefäß mit Hilfe einer Zentrifugalpumpe, einer sogenannten MC-Pumpe, erzeugt wird.

5 15. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Peroxidbleiche hydraulisch, ohne daß im Bleichgefäß eine Gasphase zugegen ist, durchgeführt wird.

10 16. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Durchmesser des Bleichgefäßes 3 Meter, vorzugsweise 5 Meter und mehr bevorzugt 7 Meter übersteigt.

17. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Mangangehalt weniger als 5g/BDTM Zellstoff, bevorzugt weniger als 1 g/BDTM Zellstoff, und mehr bevorzugt wertiger als 0,5 g/BDTM Zellstoff in dem der Peroxidstufe zugeführten Zellstoff beträgt, welcher Gehalt weitgehend derselbe ist wie der Gehalt in dem fertig gebleichten Zellstoff.

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### Revendications

- Procédé de blanchiment sans chlore de pâte chimique en association avec sa production, dans lequel une suspension de la pâte possède une concentration dépassant 8% de matière fibreuse cellulosique, dans lequel une pâte entrant dans une chaîne de blanchiment est chargée en continu à travers au moins un récipient de blanchiment dans la chaîne de blanchiment, est traitée avec au moins un acide pour ajuster le pH à une valeur inférieure à 7, et avec un chélateur, et est ensuite blanchie en au moins une étape jusqu'à une blancheur dépassant 80% ISO, avec du peroxyde d'hydrogène ou une quantité correspondante d'un autre peroxyde, employé en une quantité dépassant 5 kg/BDMT, caractérisé en ce que le blanchiment au peroxyde est réalisé à une température supérieure à 90°C et à une pression, dans le récipient de blanchiment, supérieure à 2 bars, et en ce que la section droite du récipient de blanchiment dépasse 3 m<sup>2</sup>, et en ce que l'aire de la surface de métal exposée vers l'intérieur du récipient de blanchiment est inférieure à 4V m<sup>2</sup>, où V indique le volume du récipient en m<sup>3</sup>.
- Procédé selon la revendication 1, caractérisé en ce que, en conjonction avec le blanchiment, de l'oxygène est ajouté en une quantité inférieure à 5 kg/BDMT, de préférence inférieure à 3 kg/BDMT, mieux encore inférieure à 1 kg/BDMT.
- Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que la température durant le blanchiment est égale ou supérieure à 100°C et, mieux encore, est comprise entre 100°C et 105°C.
- Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que la quantité de peroxyde employée dépasse 10 kg/BDMT et est inférieure à 35 kg/BDMT pour permettre l'obtention d'une blancheur supérieure à 85 ISO.
- Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que la pression dépasse 3 bars, de préférence est située dans l'intervalle de 5 à 15 bars et, mieux encore, est située dans l'intervalle de 5 à 10 bars.
- Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que l'on ne laisse pas la suspension de pâte, durant le blanchiment, entrer en contact, dans une mesure significative, avec les surfaces métalliques, de préférence au moins la surface interne du récipient de blanchiment étant faite d'une matière polymère ou céramique.
- Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que l'étape Q avec le chélateur est précédée d'une étape Z ou d'une étape à l'acide peracétique et en ce que l'on obtient une blancheur dépassant 85 ISO en utilisant un tel procédé à 2 étapes, en association avec une consommation de peroxyde inférieure à 20 kg/BDMT.
- Procédé selon la revendication 7, caractérisé en ce qu'aucun lavage n'a lieu entre ZQ et, de préférence, en ce qu'une étape A avec un acid précède l'étape Z.
- Procédé selon la revendication 3, caractérisé en ce que, à l'étape de blanchiment, on ajoute d'abord à la pâte un agent élévant le pH avant d'y mélanger le peroxyde, à une température inférieure à 90°C, avant d'élèver finalement la température à la valeur voulue pour réaliser le blanchiment proprement dit.

10. Procédé selon la revendication 9, caractérisé en ce que, lors de l'addition de l'agent élévant le pH à la suspension de pâte dans l'étape de blanchiment, le pH initial est élevé à pas plus de 11,5, de préférence à une valeur comprise entre 10 et 11.

5 11. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce qu'au moins un agent complexant participe à l'étape de blanchiment au peroxyde, cet agent complexant étant de préférence ajouté à la suspension avec le peroxyde.

10 12. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que l'un dudit ou desdits agents complexants est un agent supportant essentiellement un pH allant jusqu'à 11, cet agent complexant étant de préférence le DTPA.

15 13. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le DTPA est ajouté en une quantité de préférence comprise entre 1 et 2 kg de DTPA/ADMT.

14. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que la pression positive dans le récipient de blanchiment s'obtient à l'aide d'une pompe centrifuge, appelée pompe MC.

● 15. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le blanchiment au peroxyde est réalisé par voie hydraulique, aucune phase gazeuse n'étant présente dans le récipient de blanchiment.

16. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le diamètre du récipient de blanchiment dépasse 3 mètre, de préférence 5 mètres et, mieux encore, 7 mètres.

25 17. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que la teneur en manganèse est inférieure à 5 g/BDTM de pâte, de préférence inférieure à 1 g/BDTM de pâte et, mieux encore, inférieure à 0,5 g/BDMT de pâte, dans la pâte chargée dans l'étape au peroxyde, cette proportion étant globalement la même que la proportion dans la pâte finalement blanchie.

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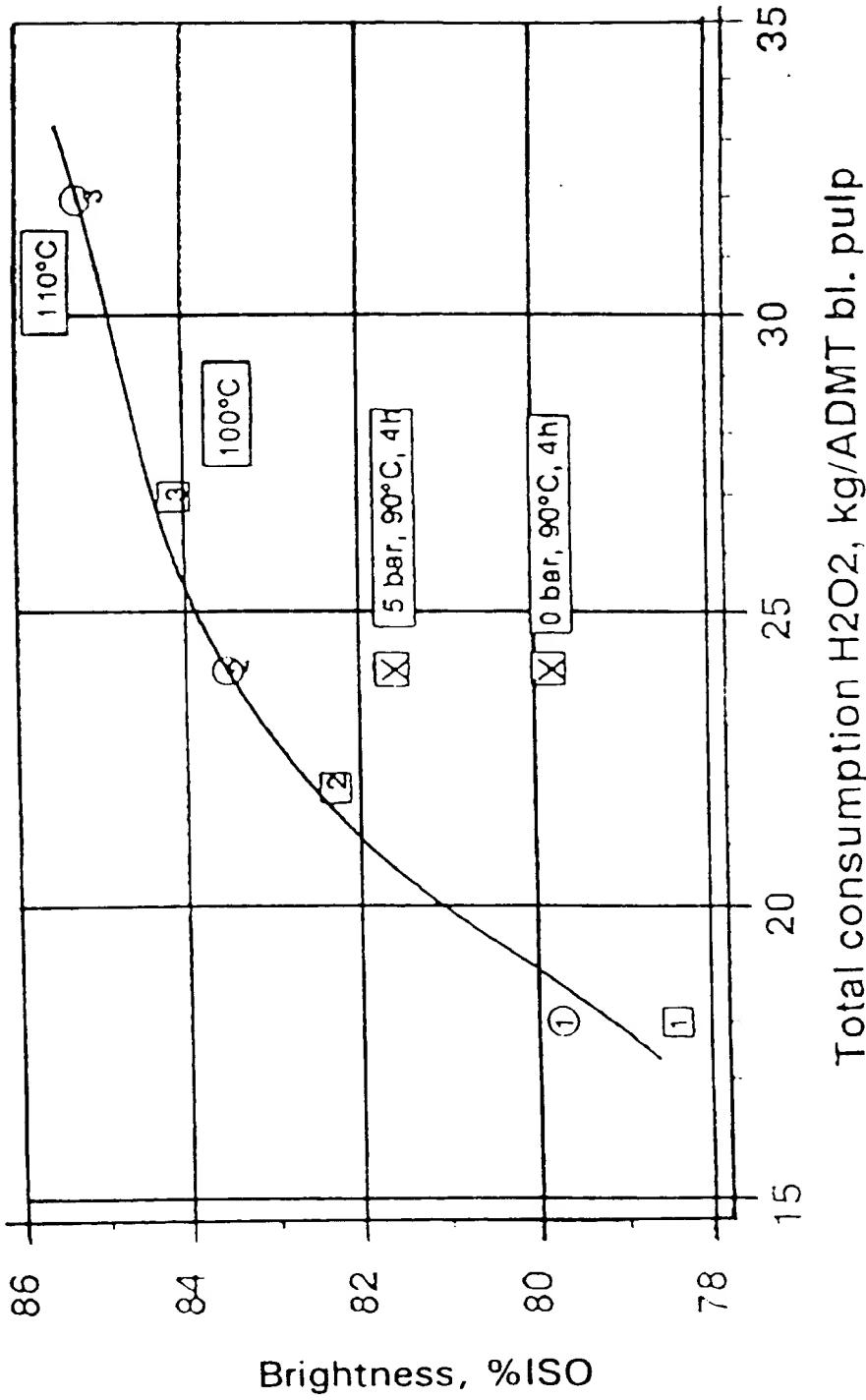
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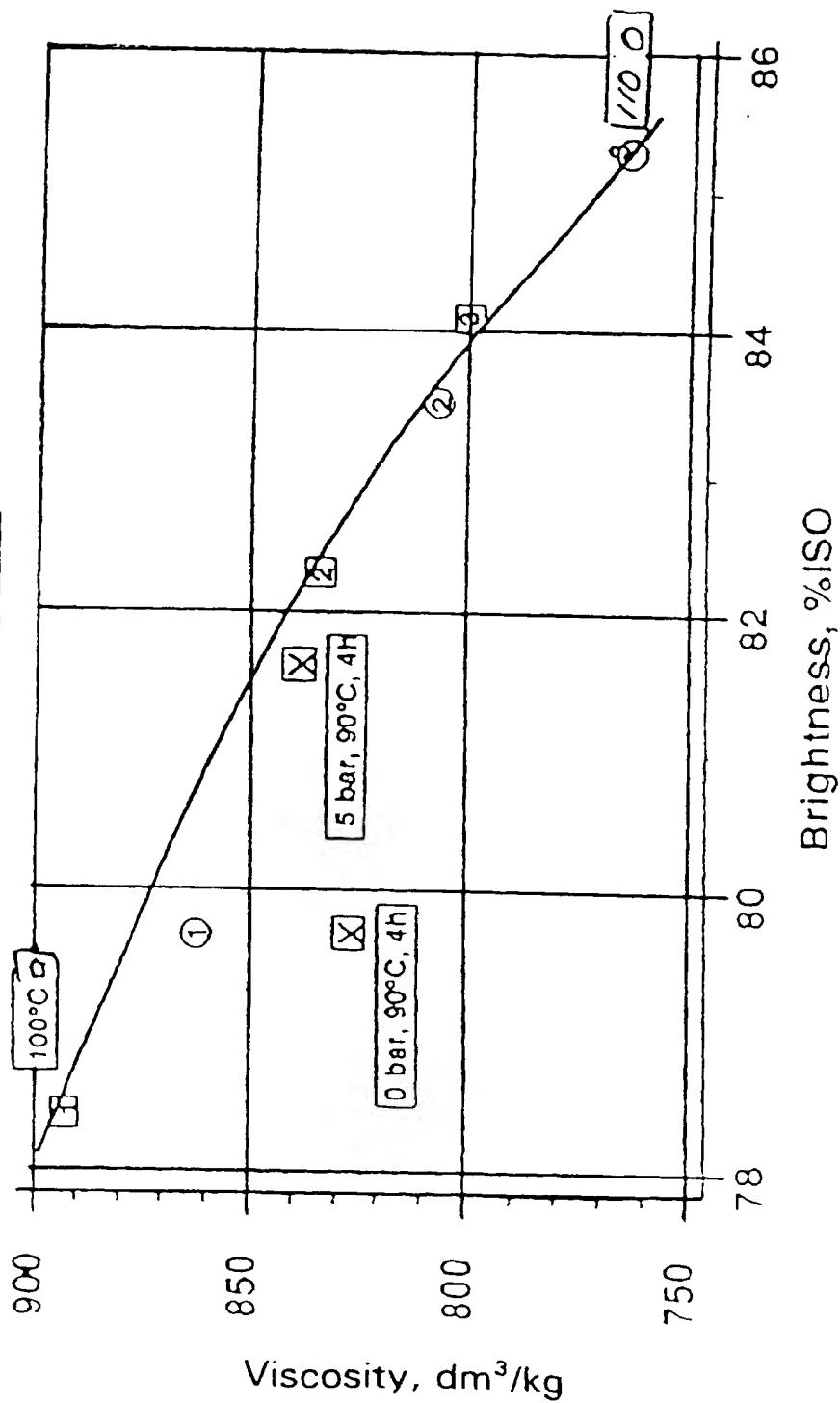
# Q(PO) bleaching of oxygen delignified mill ITC pulp

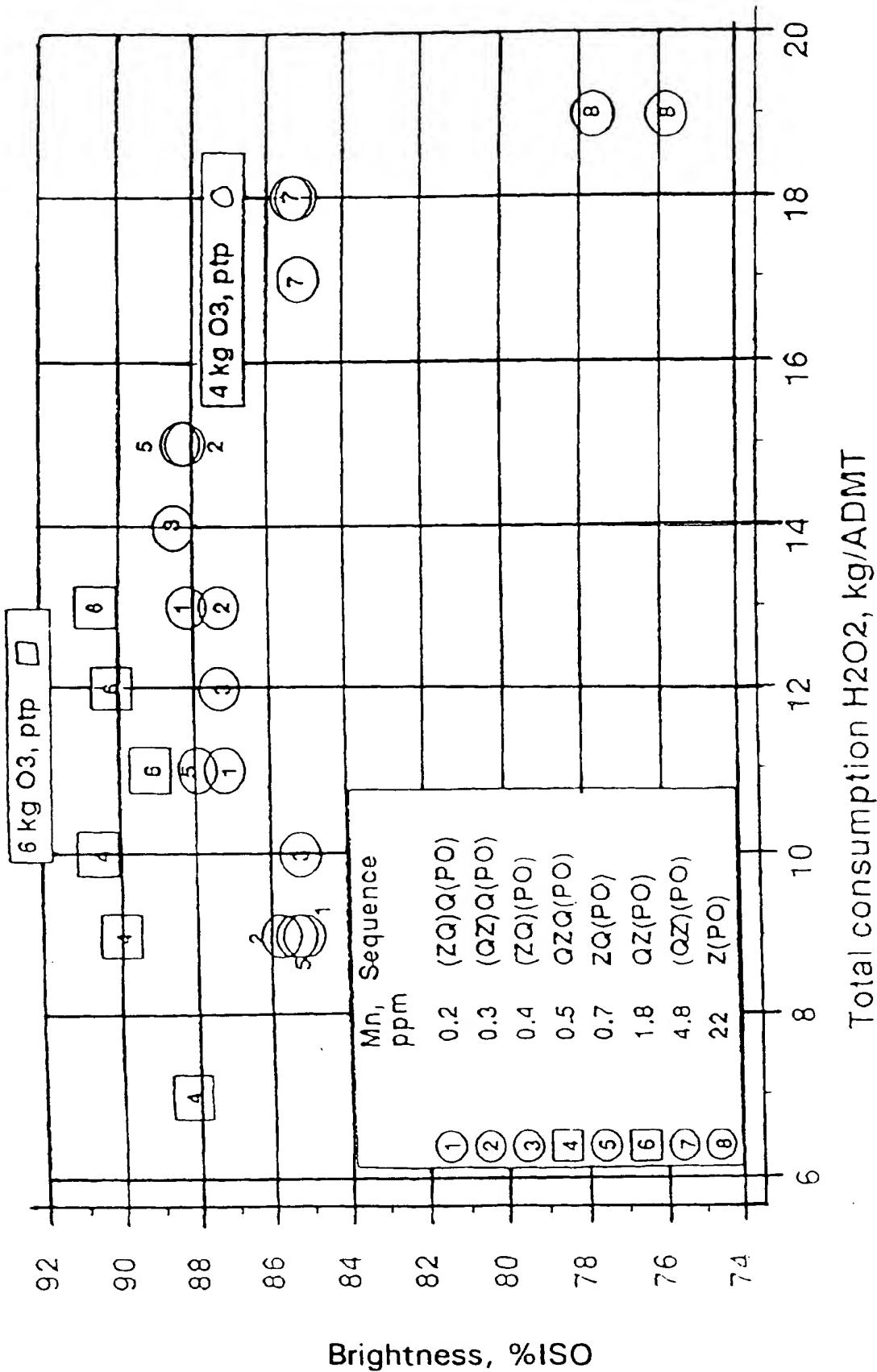
Oxy. del. pulp: Kappa No. 12.1, Visc. 1020 dm<sup>3</sup>/kg  
33 kg peroxide/pulp  
5 bar with retention times 1,2 and 3 hours

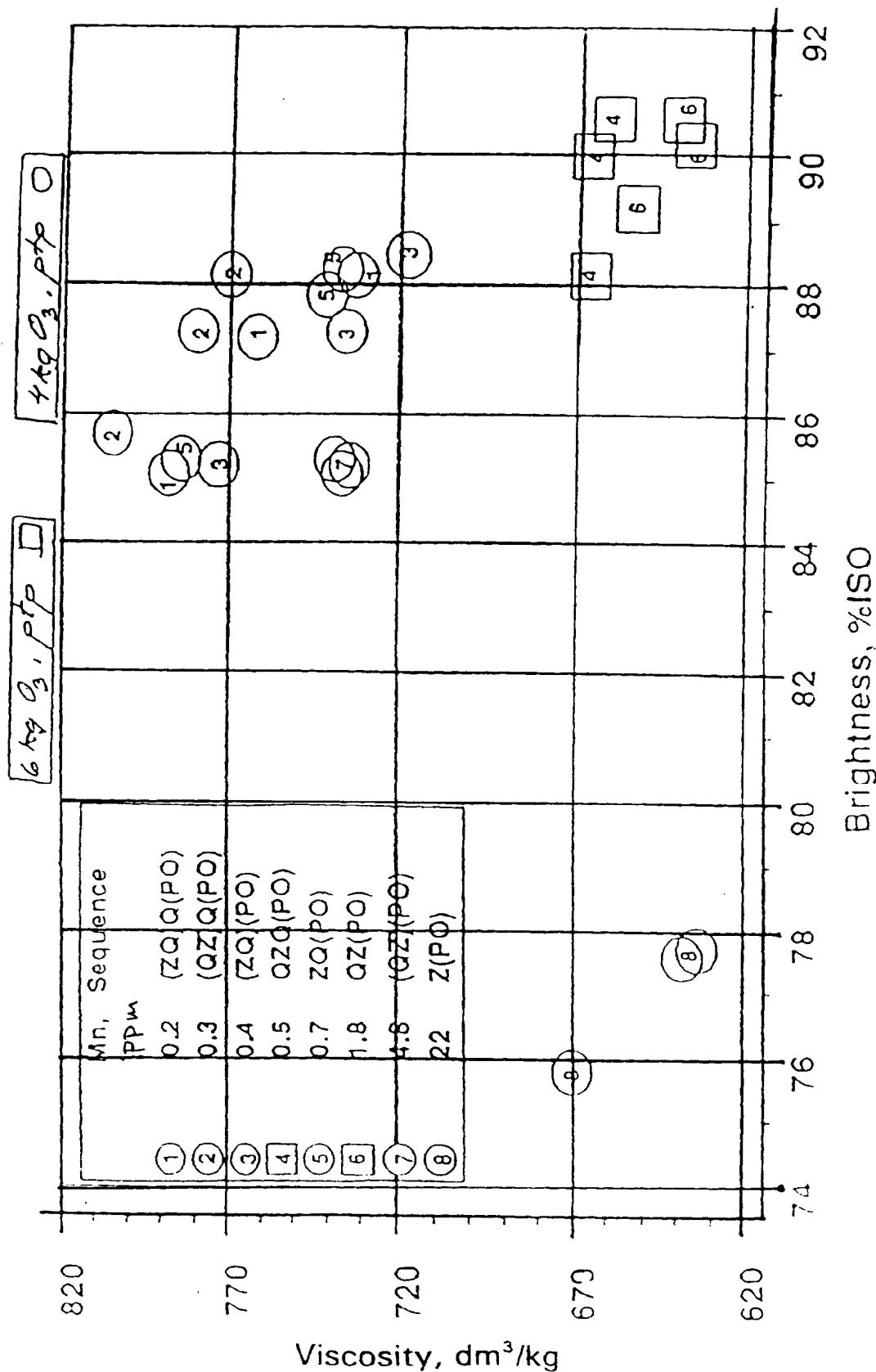


# Q(PO) bleaching of oxygen delignified mill ITC pulp

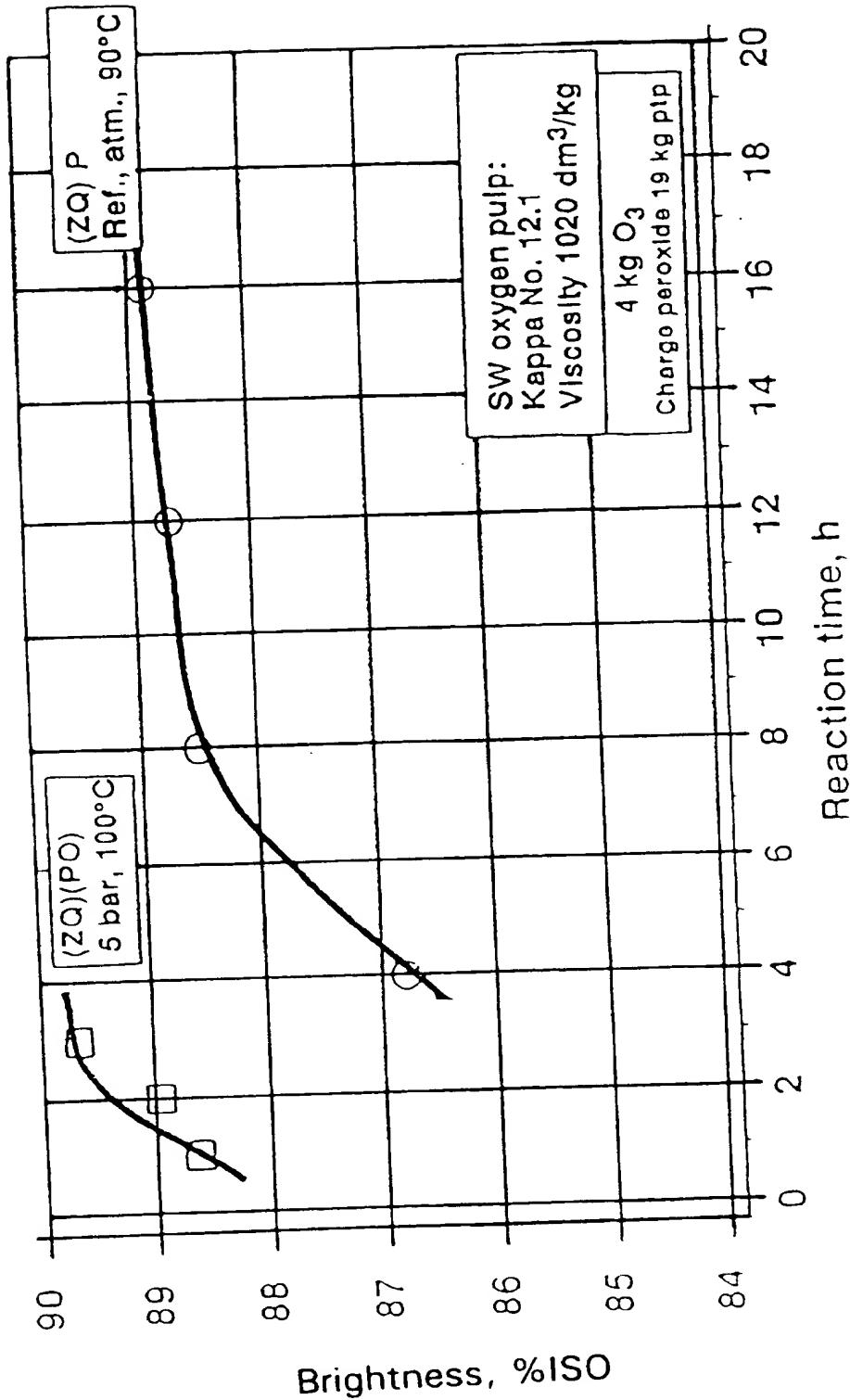
Oxy. del. pulp: Kappa No. 12.1, Visc. 1020 dm<sup>3</sup>/kg  
33 kg peroxide PTP  
5 bar with retention times 1,2 and 3 hours



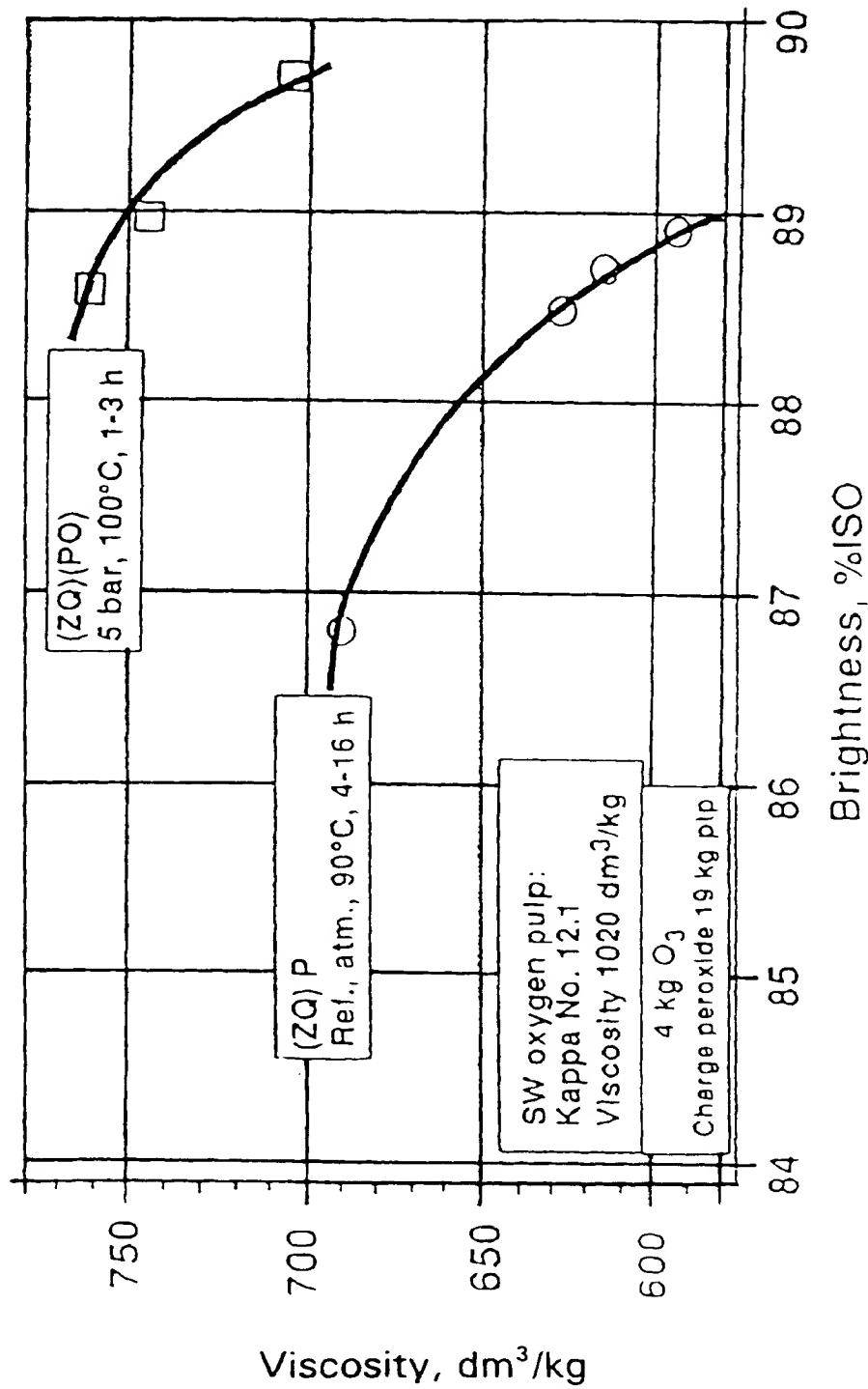




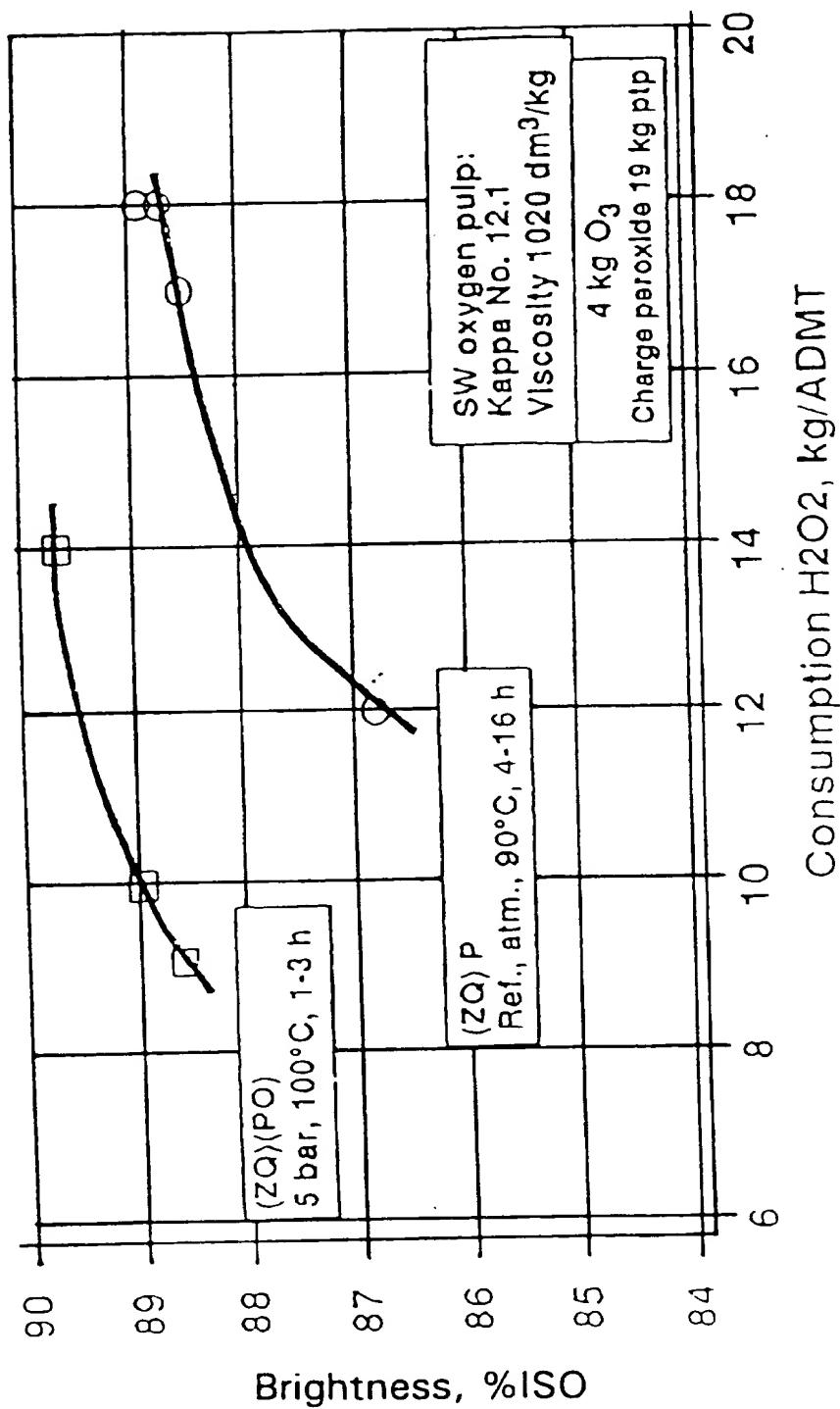
Bleaching with peroxide and ozone.  
Brightness development vs reaction time.



Bleaching with peroxide and ozone.  
Viscosity loss.

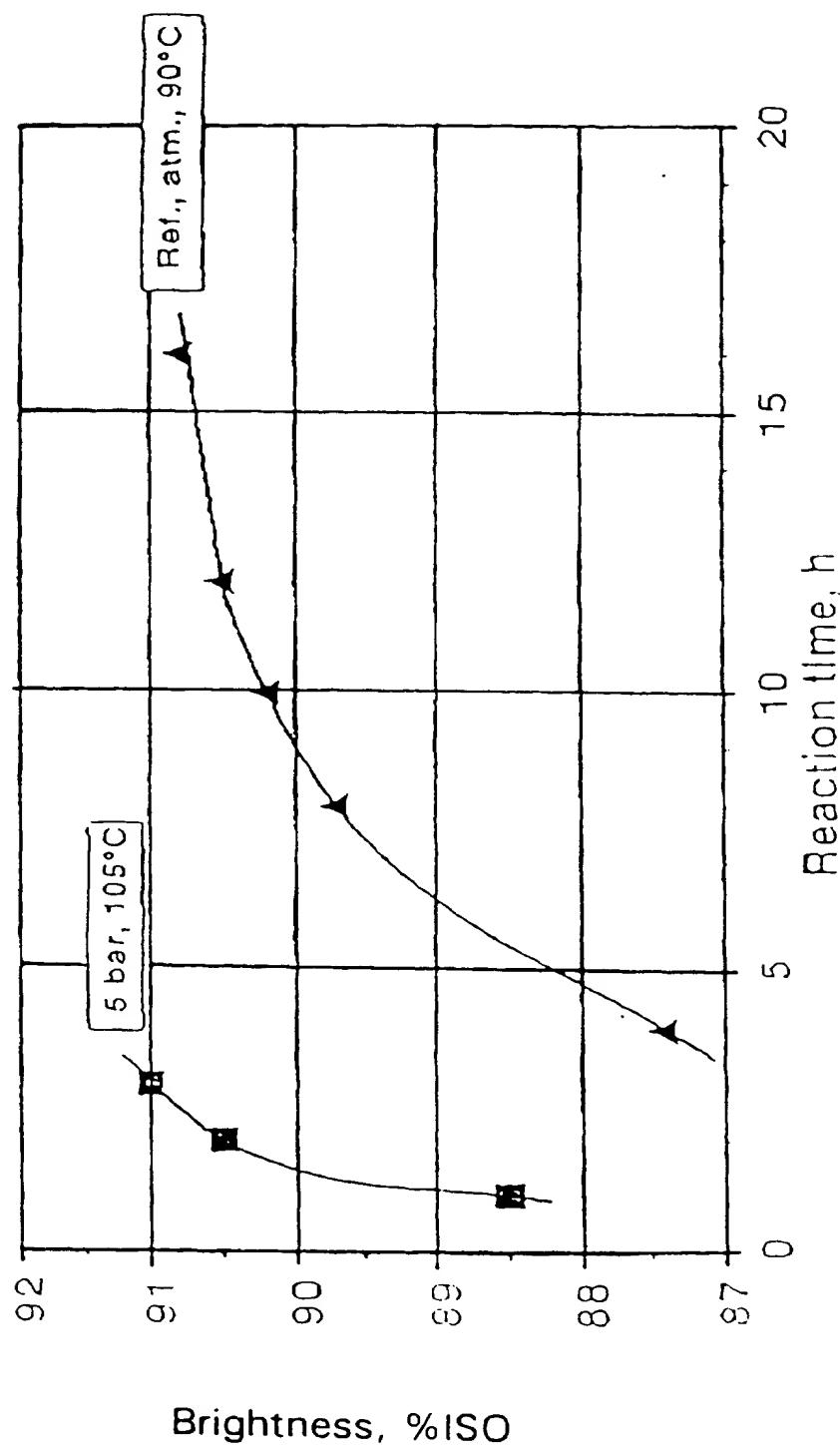


Bleaching with peroxide and ozone.  
Brightness development vs consumption of peroxide.



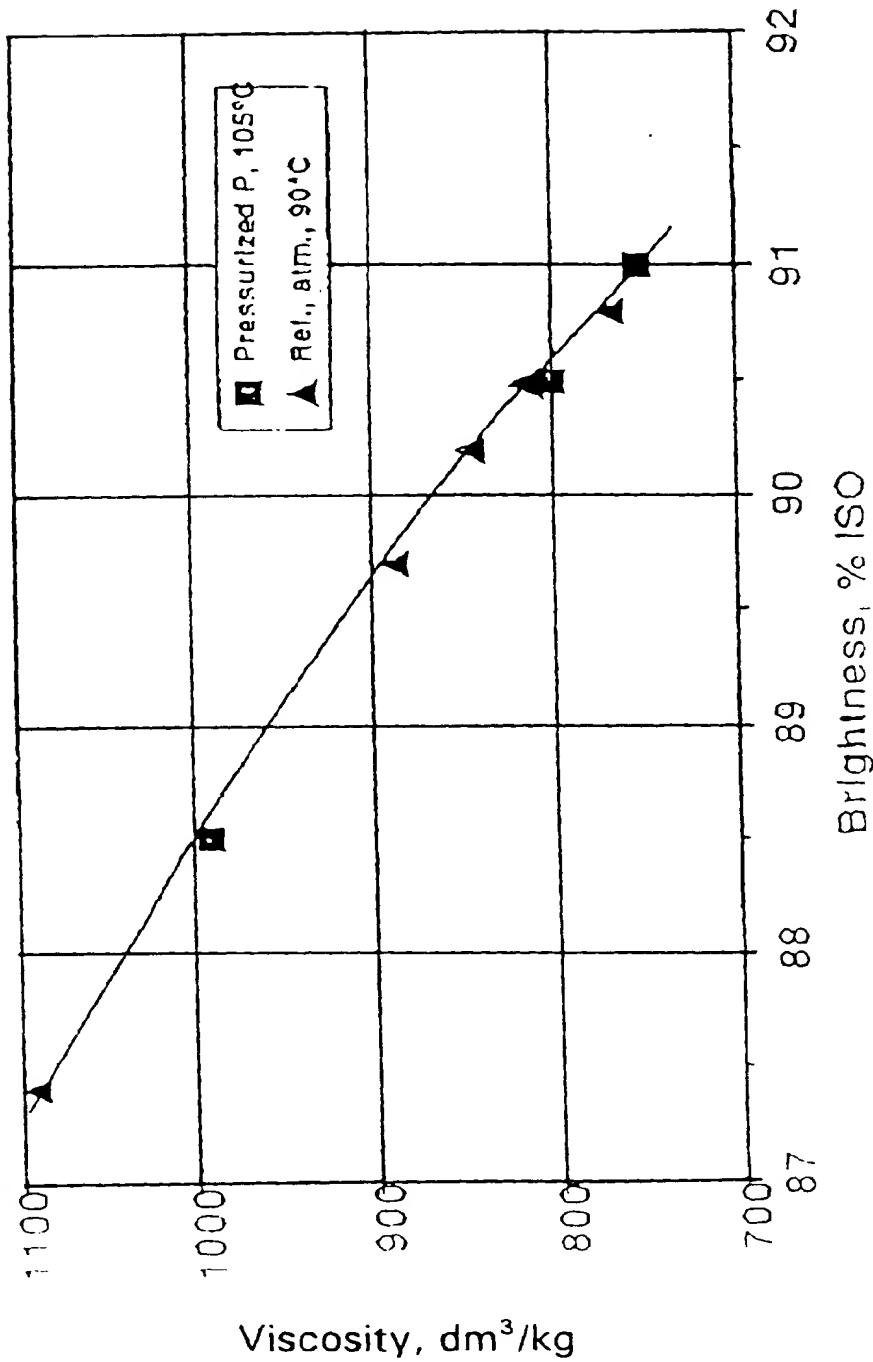
## Pressurized (PO)- bleaching of hardwood pulp.

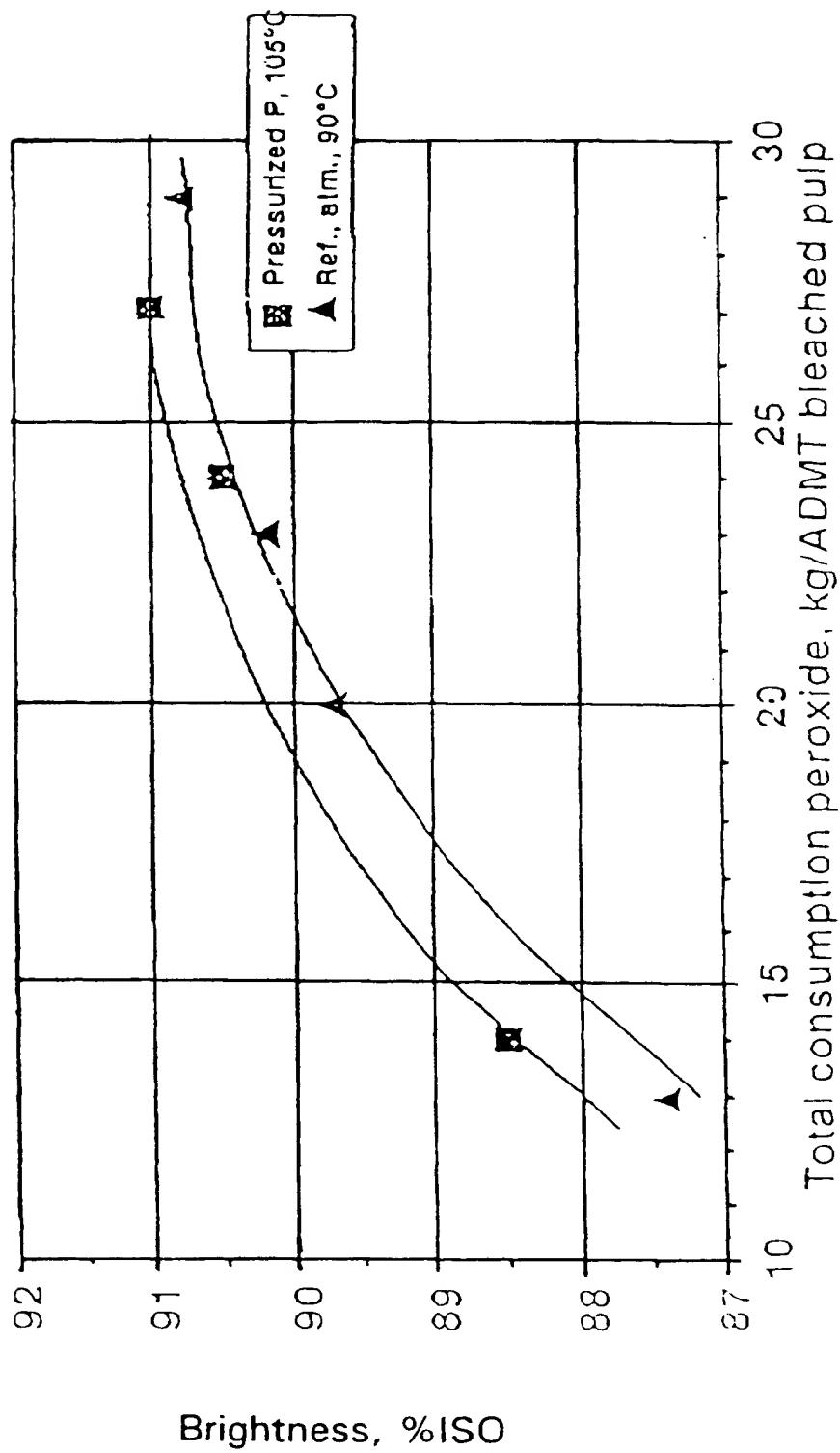
Euc. *globulus*, Oxy. del. pulp: Kappa No. 7.2  
 Q pretreatment  
 Charge peroxide: 33 kg/plp



Pressurized (PO)- bleaching of hardwood pulp.  
Influence on viscosity.

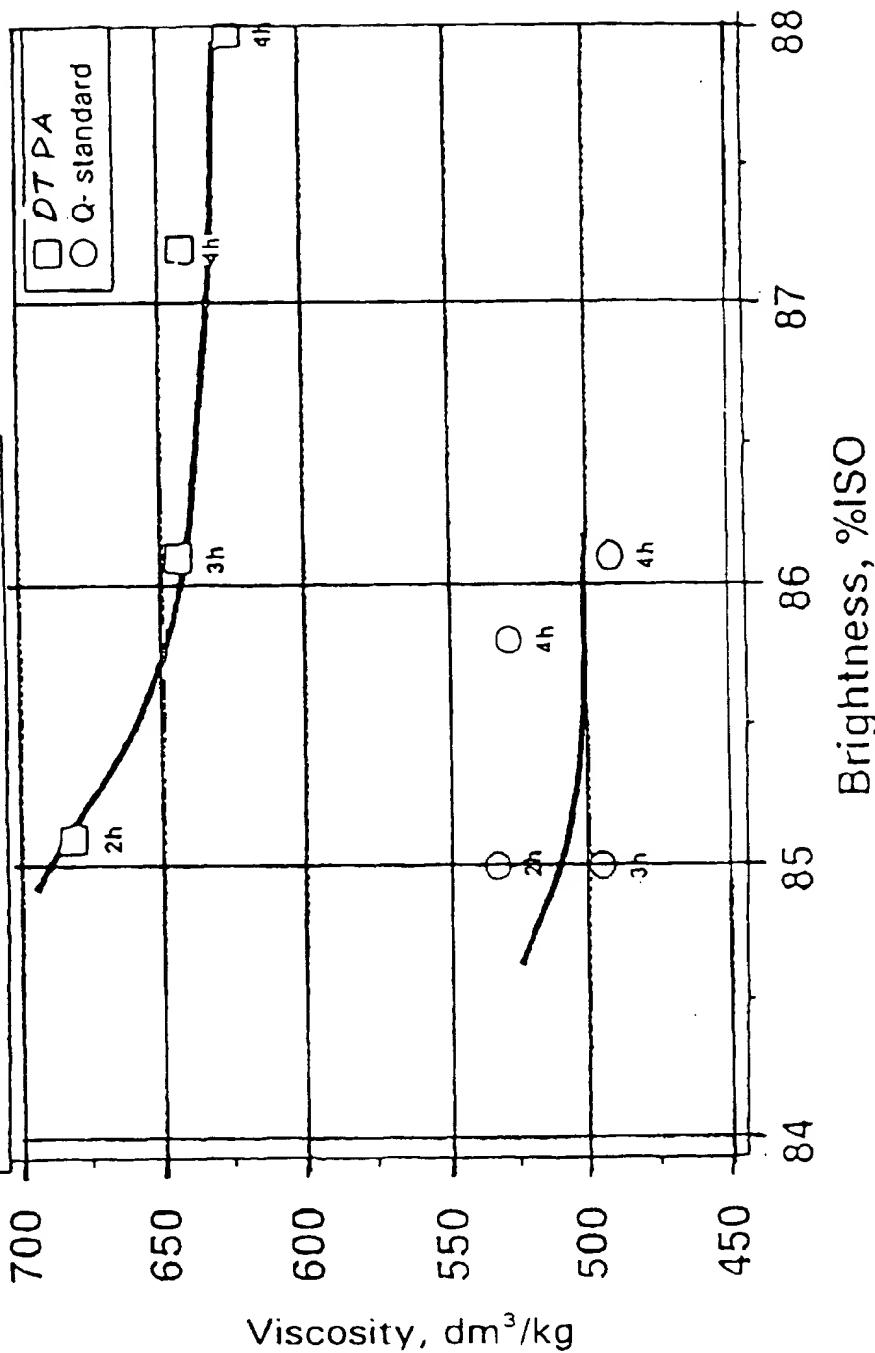
Euc. globulus, Oxy. del. pulp: Kappa No. 7.2, Visc. 1256 dm<sup>3</sup>/kg  
O pretreatment  
Charge peroxide: 33 kg/plp





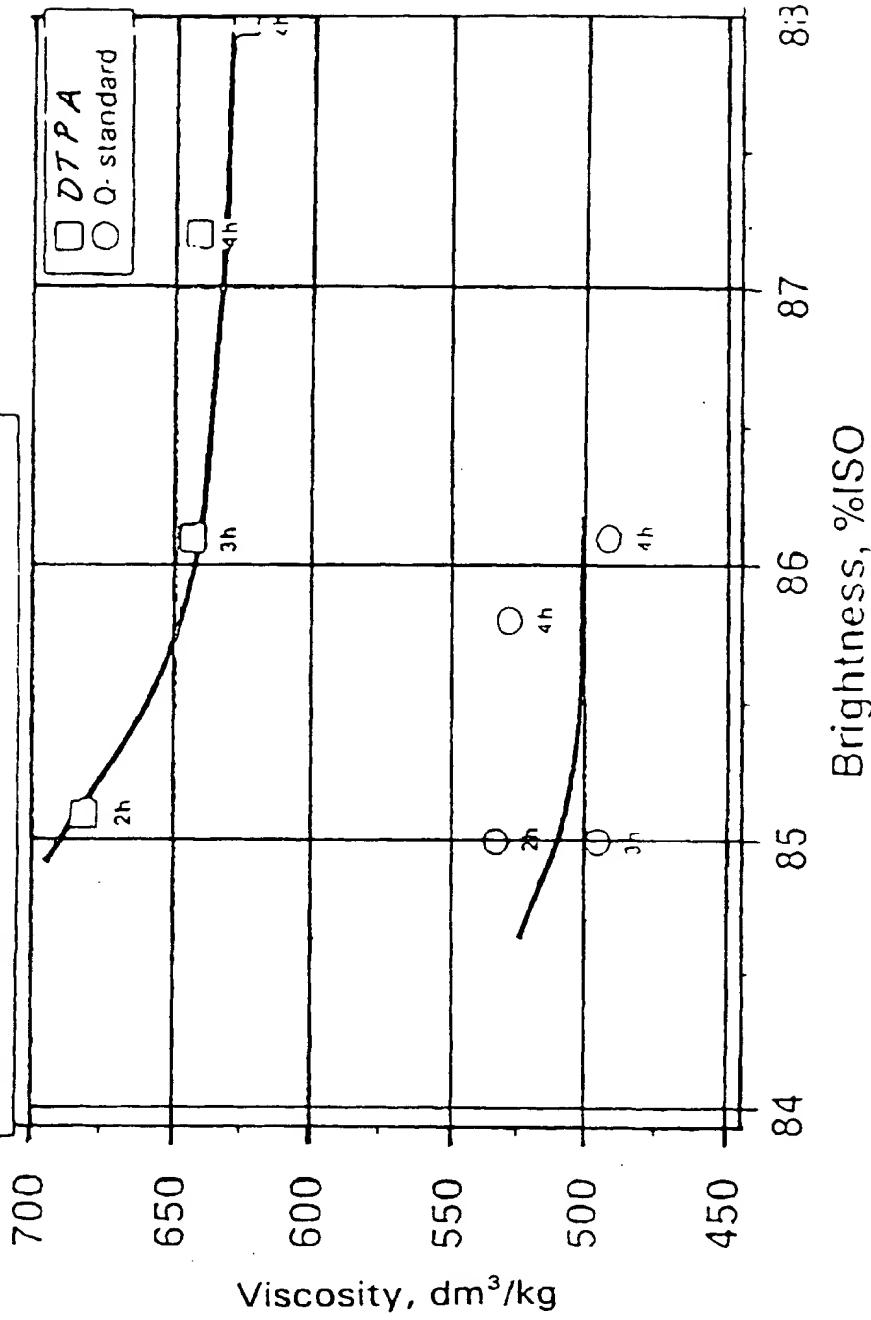
# Pressurized (PO)- bleaching of softwood Influence on viscosity

Oxy. del. pulp: Kappa No. 8.1, Visc. 808 dm<sup>3</sup>/kg  
 Pretreatment: Q- standard alt. DT PA  
 Charge peroxide: 32 kg P<sub>1</sub>P  
 Temperature: 100-105 °C  
 Pressure: 5 bar



## Pressurized (PO)-bleaching of softwood kraft pulp. Influence on viscosity

Oxy. del. pulp: Kappa No. 8.1, Visc. 808 dm<sup>3</sup>/kg  
 Prebleaching: Q-standard alt. DT PA  
 Charge peroxide: 32 kg p/p  
 Temperature: 100-105 °C  
 Pressure: 5 bar



Q(PO)-bleaching of lab. oxygen delignified  $\pi$ C SW pulp.  
 Kappa no 13.0 and viscosity 1023 dm<sup>3</sup>/kg  
 Influence of protectors in (PO)-stage

